A Study of the Composition of an Ammonium Phosphomolybdate and the Determination of Phosphorus.

DISSERTATION

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE FACULTY OF PURE SCIENCE IN COLUMBIA UNIVERSITY

BY

NORMA E. JOHANN, A.B., A.M.

New York City

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N. E. J.

A STUDY OF THE COMPOSITION OF AN AMMONIUM PHOSPHOMOLYBDATE AND THE DETERMINATION OF PHOSPHORUS

In view of the conflicting statements found in the literature regarding the composition of the ammonium phosphomolybdate precipitate, it was decided to try once more to analyse this precipitate and to determine, if possible, the conditions for obtaining a precipitate of constant composition.

Following are given some of the analyses of ammonium phosphomolybdate for phosphorus pentoxide and molybdic oxide found in the literature together with the method of treating the precipitate. In many cases the methods of analysis are not given.

Author	Method of treating ammonium phosphomolybdate precipitate	P_2O_5	MoO_3	Ratio P_2O_5:MoO_3
Nutzinger[1]	dried at 100°C.	3.82%	92.70%	1:23.92
Seligsohn[2]	dried at 100°C.	3.142	90.744	1:28.48
Sopp[3]		3.20	86.0	1:26.50
Struve & Svanberg[4]		3.63	86.88	1:23.60
Sonnenschein[5]		3.03	86.87	1:28.27
Macagno[6]	dried at 100°C.	3.142	90.744	1:28.48
Rammelsberg[7]	dried at 100°C.	3.90	86.45	1:21.85
Gibbs[8]	dried by pressing with woolen paper	3.70 & 3.83	89.00	1:23.72
Hundeshagen[9]	washed with dilute HNO_3 dried at 130-150°C.	3.72 &	91.86	1:24.35
Babbitt[10]	washed with water, dried at 85-90°C. for 3 days	3.77 3.724	92.11 90.315	24.10 1:23.92
Doolittle & Eavensen[11]	dried to constant weight at 130°C.	3.76	91.65	1:24.00

[1]Jahresb, 1855, 374.
[2]J. f. Prakt. Chem. *67*, 470.
[3]Pogg. Annal. *109*, 136.
[4]Jahresb, 1847, 412.
[5]J. f. Prakt. Chem. *53*, 342 (1851).
[6]Chem. News *31*, 197 (1875).
[7]Ber. *10*, 1776 (1877).
[8]Am. Chem. Jour. *3*, 317 (1881).
[9]Z. f. Anal. Chem. *28*, 141, (1889).
[10]J. Anal. and Appl. Chem. *7*, 165 (1893).
[11]Jour. Am. Chem. Soc. *16*, 234 (1894).

Blair & Whitfield[12] dried at 100°C. for 12 hours	3'59	88.06	1:24.19
dried over KOH for 3 months	3.59	88.06	1:24.19
Gladding[13] washed with 1% HNO_3, dried to constant weight at 105°C	3.76	91.36	1:23.96
Baxter[14] washed with 10% NH_4NO_3, heated to constant weight at 300°C.	3.7422	92.16	1:24.29

Hundeshagen says that the composition of the precipitate after washing with cold dilute nitric acid and drying at 130-150°C. corresponds to the formula $(NH_4)_3PO_4 . 12\ MoO_3$ whether precipitated in nitric, hydrochloric or sulphuric acid solutions containing ammonium salts. The precipitate obtained with excess acid, washed with cold dilute acid and dried in a desiccator contains, according to the acid, two molecules of HNO_3 or HCl with one molecule of H_2O probably in unstable chemical combination. This formula $(NH_4)_3PO_4 . 12\ MoO_3$ of the dried precipitate is the one now most generally accepted. It corresponds to 3.783% P_2O_5 and 92.06% MoO_3.

Finkener (Ber. *11*, 1638 (1878) was one of the first to point out that the ratio of P_2O_5 to MoO_3 is 1:24 and not 1:20 as given by Debray (Chem. News *17*, 183 (1868) or 1:22 as given by Rammelsberg. He and also Auld (Analyst *37*, 130 (1912) state that the variation in composition is due to variation in the amount of ammonia and water in the molecule. The work of the present investigation confirms this statement. Wolcott Gibbs believed that there are three classes of phosphomolybdates. He prepared and analysed three in which the ratio of P_2O_5 to MoO_3 was 1:20, 1:22, 1:24. It may be possible to have a mixture of the three classes of salts. Hissink and von der Waerden (Chem. Weekblad *2*, 179 (1905) have proposed a formula requiring 12.65 molecules of MoO_3 per molecule of phosphomolybdate and Wardlaw (J. Pro. Roy. Soc. N. S. Wales*48*, Part I, 73 (1914), 12.75.

A large number of investigators have determined phosphorus by weighing either the dried precipitate $(NH_4)_3PO_4 . 12\ MoO_3$ or the compound $P_2O_5 . 24\ MoO_3$, obtained by ignition of the phosphomolybdate under various conditions. Following are some of the factors given for these procedures.

[12]Jour. Am. Chem. Soc. *17*, 747 (1895).
[13]Jour. Am. Chem. Soc. *18*, 23 (1896).
[14]Am. Chem. Jour. *28*, 298 (1902).

Author	Method of treating precipitate	Factor to P_2O_5
Finkener[15]	washed with NH_4NO_3, heated to 160-180°C.	0.03794
Hehner[16]	washed with alcohol, dissolved in NH_4OH evaporated solution, dried at 100°C.	0.03509
Tamm[17]	washed with 1% HNO_3, dried at 120°C.	0.0376
Wood[18]	washed with dilute HNO_3, dried at 100°C.	0.0373
	ignited	0.0396
Carnot[19]	washed with H_2O, dried at 100°C.	0.0373
Villiers & Borg[20]	dried at 100°C. for 6 hrs.	0.03728
Meineke[21]	washed with H_2O, alcohol, ether, and ignited	0.03949
Gladding[13]	washed with 1% HNO_3, dried at 105°C.	0.0376
Woy[22]	washed with 1% NH_4NO_3 + HNO_3, ignited → $P_2O_5 \cdot 12MoO_3$	0.03946
Lorenz[23]	washed with 2% NH_4NO_3, alcohol, ether, dried in vacuum	0.03295
Baxter[14]	washed with 10% NH_4NO_3, heated to constant weight at 300°C.	0.03742
Raben[24]	washed with alcohol, dried at 110-120°C.	0.0375
Christensen[25]	ignited—assumed $P_2O_5 \cdot 24MoO_3$	0.0394
Jörgensen[26]	heated, not too strongly to $P_2O_5 \cdot 24MoO_3$	0.0394
Chesneau[27]	dried at 105°C.	0.0366
	ignited	0.0387
Maude[28]	ignited	0.039467
Auld[29]	washed with 1% HNO_3, dried, ignited to constant weight	0.0396
Neubauer & Lücker[30]	washed with 2% NH_4NO_3, acetone	0.03295

The wide variation in the factors proposed even when the conditions are nearly identical and the many conditions of treatment which have been suggested show conclusively that analysts have encountered difficulties in the application of those procedures involving the drying or ignition of the phosphomolybdate precipitate.

With a view to overcoming some of the difficulties and uncertainties of the gravimetric method, various volumetric procedures

[15]Ber. *11*, 1638 (1878).
[16]Analyst *4*, 23 (1879).
[17]Chem. News *49*, 208 (1884).
[18]Jour. Anal. Chem. *1*, 138 (1887).
[19]Chem. News *67*, 101 (1893).
[20]Comptes Rendus *116*, 989 (1893).
[21]Chem. Ztg. *20*, 108 (1896).
[22]Chem. Ztg. *21*, 441 (1897).
[23]Z. f. Anal. Chem. *46*, 193 (1907).
[24]Z. f. Anal. Chem. *47*, 546 (1908).
[25]Z. f. Anal. Chem. *47*, 529 (1908).
[26]Z. f. Anal. Chem. *46*, 370 (1907).
[27]Comptes Rendus *146*, 758 (1908).
[28]Chem. News *101*, 241 (1910).
[29]Analyst *37*, 130 (1912).
[30]Z. f. Anal. Chem. *51*, 161 (1912).

have been proposed. The method most generally used is an acidimetric one in which the phosphomolybdate precipitate washed free of acid is dissolved by the addition of a measured excess of standard alkali and the excess is titrated back with standard acid. Here again wide variation is encountered in the statements of the authors as to the numbers of moles of alkali equivalent to one mole of phosphomolybdate precipitate. The values most frequently given are 23, 26 or 28 moles of alkali per mole of precipitate.

Thilo (Chem. Ztg. *11*, 193 (1887) dissolved the yellow precipitate in ammonium hydroxide titrated back with sulphuric acid using litmus as indicator. His ammonium hydroxide solution contained 32 g. NH_3 per liter when 1 cc. was equivalent to .0669 g. of precipitate. Rothberg and Auchinvole (J. Anal. and Appl. Chem. *6*, 243 (1892) washed the precipitate with 1% nitric acid solution, then with potassium nitrate to remove the free acid, dissolved it in a standard sodium hydroxide solution and titrated back the excess with nitric acid using phenolphthalein as the indicator. Manby (J. Anal. and Appl. Chem. *6*, 82 (1892) and Handy (J. Anal. and Appl. Chem. *6*, 204, (1892) used this same method, standardizing their alkali against the pure precipitate or a steel of known phosphorus content. Pemberton (J.A.C.S. *15*, 382 (1893), *16*, 278 (1894) was the first to make an extended investigation of this method. He agrees with Hundeshagen that 23 molecules of alkali are required for one molecule of ammonium phosphomolybdate. Kilgore (J.A.C.S. *16*, 765 (1894), *17*, 950 (1895) modified Pemberton's method in that he precipitated the phosphomolybdate at 60°C. instead of at boiling temperature as Pemberton did. Kilgore washed the precipitate with 1% nitric acid solution, then with a 3% potassium nitrate solution and finally with water. He dissolved the precipitate in standard potassium hydroxide solution and titrated back the excess with nitric acid using phenolphthalein as the indicator. Various other modifications of the Pemberton-Kilgore method have been suggested.

Lagers (Z. f. Anal. Chem. *47*, 561 (1908) believes that the formula for the ammonium phosphomolybdate precipitate is $(NH_4)_3PO_4 \cdot 12.65\ MoO_3$ which requires 24.30 molecules of sodium hydroxide for neutralization.

The existing uncertainty of the composition of the phosphomolybdate precipitate and the conflicting statements found in regard to the volumetric method, make this volumetric method unsatisfactory as well as the direct gravimetric method. One difficulty in the

volumetric method is that the end-point is not sharp. This may be due to several causes, as, for instance, the ammonia or phosphate present in the solution of the ammonium phosphomolybdate precipitate.

The presence of ammonia was believed to cause interference with the end-point when phenolphthalein is used as the indicator by Neumann (Z. Physiol. Chem. *37*, 115 (1903), who obtained correct results only when he dissolved the precipitate in sodium hydroxide solution, boiled out the ammonia and then titrated back the excess alkali with sulphuric acid using phenolphthalein as the indicator. In this case one molecule of phosphorus pentoxide was equivalent to 56 molecules of sodium hydroxide.

Neumann's method has been found unsatisfactory by some authors among whom are Gregersen (Z. Physiol. Chem. *53*, 453 (1907), Taylor and Miller (J. Biol. Chem. *18*, 215 (1914), and Kleinmann (Biochem. Zeitschr. *99*, 19 (1919). Falk and Sugiura (J.A.C.S. *37*, 1507 (1915) also studied Neumann's method. They remove the ammonia either by boiling or by adding formaldehyde. Heubner (Biochem. Zeit. *64*, 393 (1914) used Neumann's method with Gregersen's modification. These authors give the factor 1 cc. $n/2$ NaOH is equivalent to 0.553 mg. phosphorus (theoretical) while Heubner used 0.57. Jodidi (J.A.C.S. *37*, 1708 (1915) also used Gregersen's modification giving 0.57 as the factor.

Wardlaw (J. Pro. Roy. Soc. N. S. Wales *48*, Part I, 73 (1914) makes the statement, which the present investigation confirms, that neither Neumann's method nor any one of the modifications gives correct results. The amount of phosphorus calculated from an acidimetric titration is in every case too high, the error increasing with the amount of phosphorus present.

The object of the present investigation is, therefore, to make a more accurate determination of the composition of the ammonium phosphomolybdate precipitate, to determine the conditions for obtaining a precipitate of constant composition, to establish the proper conditions for the acidimetric method and thus to propose the best method for the determination of phosphorus. The investigation will be presented under the following headings: Preparation of Materials; Composition of the Ammonium Phosphomolybdate Precipitate, (*a*) The Molecular Ratio of phosphorus pentoxide to molybdic oxide, (*b*) The Presence of Acid in the Molecule; New Method for the precipitation of Ammonium Phosphomolybdate; Volumetric Method.

PREPARATION OF MATERIALS

Potassium dihydrogen phosphate, KH_2PO_4.

As a standard substance for obtaining a known weight of phosphorus, potassium dihydrogen phosphate was used. This salt was chosen because it can easily be recrystallized, it contains no water hydration, and can be dried to constant weight giving a definite compound, KH_2PO_4. Its purity can also be tested by igniting a given weight to metaphosphate. The commercial salt was recrystallized several times and dried at 110°C. Portions of known weight were then ignited to metaphosphate with the following results:

Weight of KH_2PO_4	Weight of KPO_3 calculated	Weight of KPO_3 found	Difference
4.2054 g.	3.6489 g.	3.6480 g.	—.0009 g.
3.5075	3.0434	3.0425	—.0009
3.8746	3.3619	3.3613	—.0006

Molybdic oxide, MoO_3.

Due to the uncertainty of the formula of ammonium molybdate and to the volatility of molybdic oxide at the temperature of the decomposition of ammonium molybdate, it is not possible to obtain a known weight of molybdic oxide from a given weight of ammonium molybdate. It was therefore necessary, for the purpose of mixing known weights of phosphate and molybdic oxide, to prepare the latter. This was done by treating small portions of pure ammonium molybdate with concentrated nitric acid in a porcelain crucible, evaporating to dryness and igniting gently with a Bunsen flame. More nitric acid was then added and the evaporation and ignition repeated whereupon pure MoO_3 was obtained.

Molybdate precipitating reagent.

The usual molybdate precipitating reagent was not used for reasons given later. In all the precipitations of phosphorus here described the precipitating reagent was prepared by dissolving 100 grams of ammonium para molybdate in 400 cc. of water and 80 cc. of concentrated ammonium hydroxide. A second solution was prepared consisting of 400 cc. of concentrated nitric acid and 600 cc. of water. The required quantity of solution I was poured into the corresponding quantity of solution II just before using.

Ammonium phosphomolybdate.

The yellow precipitate, ammonium phosphomolybdate, was prepared by precipitating the phosphorus in a solution of potassium

dihydrogen phosphate with ammonium molybdate solution in the presence of ammonium nitrate, washing with 1% nitric acid solution, dissolving the precipitate in ammonium hydroxide and reprecipitating with nitric, hydrochloric or sulphuric acid three times. The precipitates after the first were washed with the corresponding acid and finally twice with cold water and then dried.

Washing solution.

The washing solution found most satisfactory for washing the yellow phosphomolybdate precipitate contained 10 grams of ammonium nitrate and 5 cc. of concentrated nitric acid per liter of solution.

Magnesia Mixture.

In order that both phosphorus and molybdenum could be determined in the same solution it was necessary to avoid the presence of chloride in the magnesia mixture. This reagent was therefore prepared containing acetates and an amount of magnesium equivalent to that contained in the magnesia mixture ordinarily used. For the preparation of this reagent 5.5 grams of magnesium oxide were dissolved in a slight excess of acetic acid solution. To this solution ammonium acetate was added in sufficient quantity to prevent the subsequent precipitation of magnesium in the alkaline solution finally obtained. The solution was then neutralized with ammonia and an excess equivalent to 25 cc. of concentrated ammonia was added. The volume of the solution was now brought up to 500 cc. by the addition of water.

Lead acetate solution.

For the precipitation of molybdenum as lead molybdate, a lead acetate solution was prepared by dissolving 20 grams of lead acetate in 500 cc. of water and adding sufficient acetic acid to prevent hydrolysis.

COMPOSITION OF THE AMMONIUM PHOSPHOMOLYBDATE PRECIPITATE

(a) *The Molecular ratio of phosphorus pentoxide to molybdic oxide.*

Method of Procedure: The yellow precipitate, prepared as described above, was analysed by precipitating the phosphorus with the magnesium acetate solution and the molybdenum in the filtrate with lead acetate. The method was first tested by mixing known

weights of potassium dihydrogen phosphate and molybdic oxide approximately in the proportion found in the yellow precipitate.

The molybdic oxide was dissolved in ammonium hydroxide, the potassium dihydrogen phosphate added, the solution made slightly acid with acetic acid and magnesium acetate solution added. 10 cc. of the latter were used for 20 to 25 mg. of phosphorus and the volume of the resulting solution made about 250 cc. This was heated to about 70°C., ammonium hydroxide added slowly with constant stirring until the solution was alkaline, and then 5 cc. of concentrated ammonium hydroxide added in excess. After standing six hours or longer the precipitate was filtered off, the filtrate and washing solution being caught in volumetric flask which had previously been calibrated. The precipitate was washed with 1% ammonium hydroxide solution and then dissolved in 10 to 20 cc. of 6M HCl solution. To this solution 2 cc. of magnesium acetate solution were added and the magnesium ammonium phosphate reprecipitated as above described by adding ammonium hydroxide slowly and with constant stirring. Sometimes the precipitate when first formed was gelatinous but it changed over within a short time into the crystalline form. After standing it was filtered on a procelain Gooch crucible, washed free of chlorides, ignited to constant weight and weighed as magnesium pyrophosphate. By drying the precipitate in the crucible slowly on a quartz plate over a burner, igniting slowly by means of a Bunsen burner and finally with a Meker burner a residue was obtained which was light gray. In very few cases only was the residue pure white.

The filtrate from the first precipitation was made up to a definite volume at 25°C. and portions weighed out by means of a weight burette. The density of the solution was determined at 25°C. Thus the volume of the portion taken for analysis could be calculated. This portion was taken of such a size as not to give more than 0.25 grams of precipitate. It was made slightly acid with acetic acid, 10 cc. of an ammonium nitrate solution containing 5 grams of the salt were added, and the whole diluted to 300 cc. The solution was then heated almost to the boiling point and 10 cc. of lead acetate solution added slowly with stirring. After standing twelve hours the precipitate was filtered on paper, washed with hot water, ignited gently with the Bunsen flame in a porcelain crucible and weighed as $PbMoO_4$. It was found necessary to add ammonium nitrate to the solution in order to form a precipitate of such character that it could be filtered. The following results were obtained:

P calculated from KH_2PO_4	P calculated from $Mg_2P_2O_7$	Weight MoO_3 used	MoO_3 found from $PbMoO_4$
.01634 g.	.01622 g.	0.8348 g.	0.8349 g.
.03910	.03941	1.6124	1.6125
.03233	.03264	1.8045	1.8059
.02389	.02394	1.9520	1.9501
.02487	.02475	0.9698	0.9709

The average deviation of the weight of P found from the weight used is 6 parts per 1000. The values found for MoO_3 check those used within 1 part per 1000.

Experimental Data

Portions of precipitates prepared as described above were weighed out, dissolved in ammonium hydroxide and analysed by the above method. In each case the analysis was made on a different phosphomolybdate precipitate.

Acid used for reprecipitation	Method of treating precipitate	P_2O_5	MoO_3	Ratio P_2O_5:MoO_3
HNO_3	dried with alcohol and ether,	3.56%	87.63	1:24.25
	then at 110° for 10 min.	3.56	87.33	1:24.16
HCl	dried with alcohol and ether,	3.47	85.20	1:24.22
	then at 110° for 10 min.	3.58	88.02	1:24.23
H_2SO_4	dried with alcohol and ether,	3.50	86.02	1:24.25
	then at 110° for 10 min.	3.51	86.11	1:24.20
HNO_3	dried at 110°C. for 2 hrs.	3.67	89.84	1:24.16
		3.69	90.57	1:24.20
		3.73	92.05	1:24.34
		3.73	92.30	1:24.38
HNO_3	dried over H_2SO_4 in the	3.72	91.17	1:24.16
	dark, to constant weight	3.74	91.28	1:24.09
		Mean molecular ratio....		1:24.22

Although the actual percentages found do not agree it is seen that the ratio of phosphorus pentoxide to molybdic oxide is constant, whether the precipitate is dried at 110 C., with alcohol and ether, or over H_2SO_4, and whether formed in the presence of nitric, hydrochloric or sulphuric acid. The average deviation of the above ratios is 2.5 parts per 1000. The variation in composition is therefore due to variation in the amount of other constituents in the molecules, as for instance ammonia and water, due to the method of preparing the precipitate for weighing. In most cases where the precipitate was dried at 110 C. the ammoniacal solution was slightly blue showing reduction of molybdenum to a small extent.

The molecular ratio of phosphorus pentoxide to molybdic oxide was found when a given weight of phosphorus was precipitated and the precipitate obtained was analysed.

Method of Procedure:

A number of precipitates formed under varying conditions were dried at 110° and analysed.

1. To a volume of 150 cc. containing about 47 mg. of phosphorus pentoxide, 10 cc. of concentrated sulphuric acid and 30 grams of ammonium nitrate were added. The solution was heated to 75° and 40 cc. of molybdate solution (20 cc. of the above described ammonium molybdate solution poured into 20 cc. of 8M nitric acid) added. After standing over night, the precipitate was filtered off, washed with the ammonium nitrate, nitric acid solution, dissolved in ammonium hydroxide and reprecipitated from a hot solution with nitric acid after adding 2 cc. of the molybdate solution. After standing the precipitate was filtered on a porcelain Gooch, washed with the ammonium nitrate, nitric acid solution five to six times, then twice with 1% nitric acid solution and dried to constant weight at 110°C. This precipitate was dissolved and analysed as described above.

2. Same as 1 except that the molybdate solution contained 10 grams of the salt in 100 cc. of water. Also the first precipitate was filtered on a Gooch, finally washed twice with ice cold water, dried at 110° and weighed. This precipitate was then dissolved and reprecipitated with nitric acid adding 2 cc. of the ammonium molybdate solution, filtered on a Gooch, washed with the ammonium nitrate, nitric acid solution, finally twice with ice cold water, dried at 110°C. and weighed. This precipitate was dissolved and analysed.

3. Same as 2 except that the first precipitate was dissolved and analysed.

4. In a volume of 40 cc. containing about 47 mg. of phosphorus pentoxide and 5 grams of ammonium nitrate the phosphorus was precipitated in the cold with 60 cc. of ammonium molybdate solution (20 cc. of the above described solution I poured into 40 cc. of solution II). After standing 12 hours the precipitate was filtered, washed with the ammonium nitrate, nitric acid solution, then twice with 1% nitric acid solution, dried at 110° and weighed. This was dissolved, reprecipitated with nitric acid, washed, dried and weighed as before. This precipitate was dissolved and analysed.

5. Same as 4 except that the first precipitate was dissolved and analysed.

6. Same as 4 except that 5 grams of ammonium chloride were used in place of ammonium nitrate and hydrochloric acid in place

of nitric. After standing the precipitate was filtered, washed with an ammonium chloride solution, then twice with 1% hydrochloric acid solution. After drying at 110° it was dissolved and reprecipitated with nitric acid. This precipitate was treated as in 4 then dssolved and analysed.

7. Same as 6 except that the first precipitate was dissolved and analysed.

Experimental Data

Exp.	Method	Wt. of yellow ppt. per 47 mg. of P_2O_5 taken	P_2O_5	MoO_3	Ratio P_2O_5:MoO_3
1	1	1.2755 g.	3.56%	91.60%	1:25.37
2	1	1.2850	3.55	91.57	1:25.47
3	2	1.2718	3.63	91.74	1:24.95
4	3	1.2930	3.59	91.65	1:25.17
5	3	1.2383	3.56	91.82	1:25.46
6	4	1.1693	3.62	92.52	1:25.19
7	5	1.2583	3.60	92.51	1:25.36
8	6	1.2152	3.62	92.25	1:25.12
9	7	1.2390	3.60	92.49	1:25.32
				Mean molecular ratio	1:25.27

The above results were obtained by starting with definite known weights of phosphorus pentoxide. The yellow precipitate formed in each case was dried at 110° and weighed before analysing. The wide variation in the weight of ammonium phosphomolybdate precipitate obtained from a given weight of phosphorus arises either in a variable decomposition of the precipitate during drying or in the difference in the conditions of precipitation. In all cases the surface of the dried precipitates were greenish and the ammoniacal solutions were blue. The intensity of the blue color varied.

The conditions of precipitation described except in the case of experiments 8 and 9 are similar to conditions of precipitation found in the literature. In experiments 8 and 9 chloride ion was introduced. In experiments 1, 2, 3, 6 and 8 the precipitate obtained upon reprecipitation was the one which was analysed, while in experiments 4, 5, 7 and 9 the original precipitate was analysed. Upon comparing the molecular ratio of phosphorus pentoxide to molybdic oxide it will be noticed that there is no difference obtained whether the first or second precipitate is analysed. For instance, in experiment 1 the ratio is 1:25.37 while in 7 it is 1:25.36 and in experiment 4 the ratio is 1:25.17 while in experiment 6 it is 1:25.19. Reprecipitation, therefore, does not appear to effect the composition of the precipitate.

It will also be noticed that although the percentages of phosphorus pentoxide in the yellow phosphomolybdate precipitates found are fairly constant, the precipitates vary in molybdenum content. The average deviation of these ratios, namely 5.6 parts per 1000, is larger than that found in the case of the previous precipitates formed by precipitating large amounts of phosphorus and analysing portions of the precipitates obtained. This second set of precipitates obtained from known weights of phosphorus and the whole precipitate analysed are higher in molybdenum content than the first. It was thought that this might be due to molybdenum occluded on the above precipitates. In preparing large quantities no molybdate solution was added before successive reprecipitations, while in precipitating the phosphorus from a known weight of potassium dihydrogen phosphate, 2 cc. of molybdate solution were added before precipitation.

An experiment was therefore tried where the phosphorus was precipitated according to method 4 above except that on reprecipitation no molybdate was added. The following results were obtained: 3.73% P_2O_5, 92.34% MoO_3, ratio $P_2O_5 : MoO_3$ 1 : 24.41. This ratio checks the first set obtained. From this it is evident that the precipitates obtained according to the above 7 methods contained more molybdenum than the other precipitates. If this excess of molybdenum is constant, however, no error would be introduced in a determination of phosphorus depending on the composition of the ammonium phosphomolybdate precipitate. The conditions for obtaining a precipitate of constant composition will be discussed later.

(b) The Presence of acid in the Molecule.

A great variety of formulas have been proposed for the yellow phosphomolybdate precipitate, some of which are $(NH_4)_3PO_4 . 10MoO_3$, $(NH_4)_3PO_4 . 10MoO_3 . 14H_2O$, $(NH_4)_3PO_4 . 11MoO_3$, $(NH_4)_3PO_4 . 11MoO_3 . 12H_2O$, $(NH_4)_2PO_4 . 12MoO_3$, $(NH_4)_3PO_4 . 12MoO_3 . 3H_2O$, $(NH_4)_3PO_4 . 12MoO_3 + (NH_4)_2HPO_4 . 12MoO_3 + 8H_2O$, $(NH_4)_2HPO_4 . 12MoO_3$, $(NH_4)_3PO_4 . 12.65MoO_3$, $(NH_4)_3PO_4 . 12.75MoO_3$, $(NH_4)_3PO_4 . 12MoO_3 . 2HNO_3 . H_2O$, $4[(NH_4)_3PO_4 . 12MoO_3] + (NH_4)_2SO_4 . 5MoO_3$, $8(NH_4)_3PO_4 . 12MoO_3 + (NH_4)_2SO_4 . 8MoO_3$. The last two formulas are given for precipitates formed in solutions containing large amounts of sulphate ion.

Hundeshagen (Z. f. Anal. Chem. *28*, 141 (1889), Neumann (Z. Physiol. Chem. *37*, 115 1903), Richardson (J.A.C.S., *29*, 1314 (1907), Artmann and Brandis (Z. f. Anal. Chem. *49*, 1 (1910), Falk and Sugiura (J.A.C.S. *37*, 1507 (1915) and Posternak (Compt. Rend. *170*, 930 (1920) consider that the phosphomolybdate $(NH_4)_3PO_4 . 12MoO_3$ combines in various ways with the acids or salts present in the solution to form further complexes containing nitric acid, sulphuric acid or sulphomolybdates. The arguments advanced by these authors for the formulas which they propose are as follows:

Hundeshagen states that the precipitate obtained with excess acid, washed with cold dilute acid and dried in a desiccator contains two molecules of acid with one molecule of water probably in unstable chemical combination. Both acid and water are expelled completely at a temperature exceeding 130° C. for on heating the precipitate to this temperature it lost weight giving off moist strongly acid vapors. In the case of the nitric acid compound the loss in weight was 7.13% or 7.67% on the substance dried at 150°, the hydrochloric acid compound 4.78% or 5.02% on the substance dried at 150°C. The precipitates dried in a desiccator required for neutralization two equivalents more alkali than those dried at 150° corresponding to as many equivalents of nitric or hydrochloric acid in combination with the phosphomolybdate. In point of weight two molecules of nitric acid would amount to 6.71% and two molecules of hydrochloric acid to 3.89% if referred to phosphomolybdate free from acid and water. If the numbers found as loss of weight on heating to 150° the salts previously dried in a desiccator are diminished by these amounts there remain for water 0.96% and 1.13%, of which figures the former represents exactly and the latter approximately a molecule of water. From these facts he writes the formula of the phosphomolybdate precipitate $(NH_4)_3PO_4 . 12MoO_3 . 2HNO_3 . H_2O$ or $(NH_4)_3PO_4 . 12MoO_3 . 2HCl . H_2O$ when formed in a solution containing chlorides.

Neumann accepts Hundeshagen's formula for the ammonium phosphomolybdate precipitate. The latter has shown that the two molecules of nitric acid can easily be replaced by salts or other acids present in solution. Neumann determined phosphorus in organic matter. Since in ashing sulphuric and nitric acids were present and a large amount of ammonium nitrate was added to insure complete precipitation, he believes that there can easily be a change in that part of the molecule. Such changes in composition,

however, he found have no effect on the amount of sodium hydroxide required for titration.

Richardson found that in the presence of sulphates, sulphuric acid or a sulphate was always found by analysis in the yellow phosphomolybdate precipitate. He states that it is altogether probable that a complex ammonium sulphomolybdate is formed which has the acid nature of ammonium phosphomolybdate and therefore reacts with alkali similarly to the latter.

Artmann and Brandis performed two experiments to show the effect of sulphate on the ammonium phosphomolybdate precipitate. In the first the phosphorus was precipitated in the presence of ammonium nitrate and potassium sulphate at 40°C., in the second in the presence of ammonium sulphate. In both cases the precipitates were dissolved, the ammonia distilled off and titrated, with high results. After acidifying the residues with nitric acid and adding barium chloride, precipitates of barium sulphate were obtained.

Falk and Siguira precipitated phosphorus as ammonium phosphomolybdate in the presence of sulphuric acid according to Neumann. They found that the precipitate thus formed contained sulphate as an essential part of the molecule together with excess molybdic oxide and no nitric acid. They found that the titration values were the same whether or not the precipitate was dried at 120° thus showing that no nitric acid was contained in the precipitate formed in a solution containing sulphuric acid and ammonium nitrate. They determined the amount of sulphate in the precipitate by dissolving it in ammonium hydroxide, reprecipitating with nitric acid, filtering, evaporating the filtrate to dryness after adding hydrochloric acid, taking up the residue with water, filtering and adding barium chloride to the filtrate. They thus obtained .0179 - .0214 grams of barium sulphate from precipitates from phospate solutions containing 47.1 mg. P_2O_5. Similar treatment of a corresponding solution without sulphuric acid gave .0001 and .0004 grams of barium sulphate.

Posternak prepared ammonium phosphomolybdate under varying conditions and analysed the precipitates for phosphorus, in some cases transforming them into the barium salts. He found that phosphoric acid fixes 12, sulphuric acid 8 and nitric acid 4 molecules of molybdic oxide and concludes that in acid solution a tetramolybdate is present which can combine with all mineral acids present in solution.

Other investigators do not agree with the above authors regarding the presence of acid or sulphate in the molecule of ammonium phosphomolybdate. Blair and Whitfield (J.A.C.S. *17*, 747 (1895) found that the amount of alkali required to titrate a precipitate when washed with water or dilute acid and dried over potassium hydroxide for three months was less than that required to titrate a precipitate which was dried at 150 C. from which, according to Hundeshagen, the acid would be removed. Further Fresenius (Z. f. Anal. Chem. *3*, 446 (1864) and Richters (Z. f. Anal. Chem. *10*, 440 (1871) found that sulphuric acid does not interfere with precipitation of ammonium phosphomolybdate.

The work of the present investigation shows that the presence of sulphuric acid or hydrochloric acid in solution has no effect on the precipitation of phosphorus as ammonium phosphomolybdate and that neither sulphate nor chloride is contained in the molecule under the conditions herein adopted.

Method of Procedure:

The presence of sulphate was tested for in precipitates obtained as follows: Enough potassium dihydrogen phosphate was weighed out to furnish from 46 to 68 mg. of P_2O_5. This was dissolved in water, 10 grams of ammonium nitrate added in solution, and diluted to 140 cc. To this cold solution were added 45 cc. ammonium molybdate solution. (15 cc. of the ammonium molybdate solution I poured into 30 cc. 6M H_2SO_4) and the solution stirred for a few minutes. The precipitate does not form as rapidly as in a nitric acid solution and tends to stick on the beaker. After standing over night the precipitate was filtered off and washed with the ammonium nitrate, nitric acid solution. After washing carefully with about 400 cc. of wash solution, the funnel being allowed to drain between washings, it was still possible to obtain a test for sulphate by adding barium chloride to a small amount of washings and shaking for a few minutes. The yellow precipitate was then dissolved in 10 cc. of concentrated ammonium hydroxide, 2 cc. of molybdate solution added and reprecipitated by adding nitric acid. After standing again this precipitate was filtered off, washed with the same solution as above, and the filtrate plus washings evaporated to dryness adding 5 cc. concentrated hydrochloric acid when the solution was almost dry. The residue was taken up with dilute hydrochloric acid, the molybdenum compound which separated filtered off, and 5 cc. of m/4 barium chloride solution added. After standing 24 hours the resulting barium sulphate was filtered off and weighed. Blank deter-

minations were made in a similar manner on precipitates obtained from solutions containing nitric acid in place of sulphuric acid.

Experimental results

P_2O_5 calculated from KH_2PO_4	$BaSO_4$ gms.	Wtof $BaSO_4$ per 50 mg. P_2O_5	P_2O_5 calculated from KH_2PO_4	$BaSO_4$ gms.	Wt. of $BaSO_4$ per 50 mg. of P_2O_5
.0468 g.	.0136	.0145 g.	.0536 g.	.0199 g.	.0186 g.
.0474	.0111	.0117	.0543	.0040	.0037
.0480	.0234	.0244	.0557	.0246	.0221
.0484	.0242	.0250	.0574	.0154	.0134
.0516	.0155	.0150	.0578	.0158	.0137
.0526	.0054	.0051	.0624	.0122	.0098
.0534	.0108	.0101	.0810	.0264	.0163

Blank Determinations

.0534	.0047	.0044
.0641	.0042	.0033
.0646	.0033	.0026

It will be seen that the blanks are much higher than those given by Falk and Sigiura. It is very probable that all the barium sulphate precipitates were obtained from sulphate which had not been washed out. The irregularity of results can certainly be explained by assuming the presence of varying amounts of sulphate left in or adsorbed upon the precipitate, for, as stated above, it seemed impossible to wash the precipitate free of sulphate. From these facts the conclusion was drawn that sulphate is not a part of the ammonium phosphomolybdate molecule when it is formed in a solution containing sulphate.

The presence of molybdenum was tested for in some of the above barium sulphate precipitates by fusing with sodium carbonate, dissolving in hydrochloric acid and passing hydrogen sulphide into the solution. A brown precipitate of molybdenum sulphide was obtained.

A few experiments were performed to test for the presence of hydrochloric acid in the molecule of the precipitate formed in a chloride solution. Known weights of potassium dihydrogen phosphate were dissolved in water, 5 grams of ammonium chloride added and the whole diluted to about 120 cc. To this cold solution were added 45 cc. of molybdate solution (15 cc. of the ammonium molybdate solution poured into 30 cc. of dilute hydrochloric acid containing 12 cc. of concentrated acid and 18 cc. of water) and the solution stirred. After standing 12 hours, the precipitate was filtered off

and washed with the ammonium nitrate, nitric acid solution. The precipitate was dissolved in ammonium hydroxide and reprecipitated by adding 2 cc. of molybdate solution and 15 cc. of concentrated nitric acid. The filtrate from the second precipitation was evaporated to a pasty mass, to avoid losing any hydrochloric acid which might be present, taken up with dilute nitric acid, filtered and silver nitrate added to the filtrate. Of four tested qualitatively, two gave precipitates and two none. Of the two which gave precipitates neither was as large as the blank. Another precipitate obtained by adding silver nitrate stood in the light for several weeks without showing any discoloration. The precipitates obtained were undoubtedly not silver chloride and probably contained molybdenum from the excess molybdate solution added in reprecipitation of the yellow precipitate which is shown by the large blank obtained.

A number of authors consider that either the nitric acid or the ammonium radical in ammonium phosphomolybdate or both are held in such unstable combination as to be readily replaced by various ions used in washing solutions.

Artmann (Z. angew. Chem. *26*, Aufstatzteil 203 (1913) agrees with Hundeshagen that the two molecules of nitric acid in the molecule of ammonium phosphomolybdate can be replaced by two molecules of ammonium nitrate when washing with a neutral solution of that salt.

Baxter and Griffin (A. Chem. Jour. *34*, 204 (1905) found that the ammonium was replaced by potassium. In determining ammonia, in order to decide whether molybdic oxide or ammonium molybdate was occluded on the ammonium phosphomolybdate precipitate, they washed the precipitate with potassium nitrate solution. They state "it was evident that either ammonium phosphomolybdae contains very much less ammonium than was usually supposed, or else the ammonium in the precepitate had been replaced by potassium of the washing solution. The latter explanation proved to be the correct one." Still the authors give the formula for the precipitate as $(NH_4)_2HPO_4 \cdot 12MoO_3$, only two hydrogens of phosphoric acid replaced by ammonium, and also decide that ammonium molybdate is occluded. The authors believe that the third hydrogen is replaced upon heating the yellow precipitate to 300°C. by ammonium from the ammonium nitrate which remains on the precipitate after washing with ammonium nitrate solution.

This matter was not considered worthy of investigation in the present research because since we are dealing with a crystalline pre-

cipitate such replacement, if it occurs at all, can occur only upon the surface of the crystal particles and is therefore without significance in a determination of the composition of the yellow precipitate. In view of the negative results of the experiments conducted in this research seeking to produce phosphomolybdates containing hydrochloric or sulphuric acid under the most favorable conditions for their formation it is not thought that the reactions claimed by Hundeshagen, Artmann, and Baxter and Griffin occur even at the surface of the precipitated phosphomolybdate.

NEW METHOD FOR THE PRECIPITATION OF AMMONIUM PHOSPHOMOLYBDATE

The factors which must be considered in determining the conditions for complete precipitation of phosphorus and at the same time obtaining a precipitate of constant composition are, (1) the molybdate solution, (2) the temperature of precipitation, (3) the volume and acidity of the solution before precipitation, (4) washing of precipitate. Some authors also believe that the rapidity with which the precipitating solution is added has an effect on the composition of the precipitate and also the length of time the precipitate is allowed to stand before filtering.

Molybdate solutions in great variety have been proposed. Those which have been tested in this investigation have been found unsatisfactory largely because of their instability or erratic behavior in the precipitation of ammonium phosphomolybdate. In order to overcome these defects in the reagents a radical change has been made in its preparation. By preparing this reagent in two solutions as above described, it is perfectly stable and its use in the manner described leads to definite and consistent results. Further it is sufficiently sensitive to low concentrations of phosphate ion to admit of precipitation in cold solution as a general procedure. However in the determination of phosphorus in steel, the abnormally high concentration of ferric ion interferes with the precipitation of the phosphomolybdate probably due to the formation of complexes of ferric ion and phosphate. In this case therefore it is necessary to heat the mixture to 60 C. and agitate by shaking for a few minutes under which conditions the precipitate readily forms.

The recommendations in the literature as to the temperature at which the precipitation of ammoinum phosphomolybdate is to be carried out are as varied as are those concerning the other conditions of the procedure. Woy (Chem. Ztg. *21*, 441 (1897) and

also Kleinmann (Biochem. Zeitschr. *99*, 19 (1919) precipitate at boiling temperature, Kilgore (J.A.C.S. *16*, 765 (1894); *17*, 950 (1895) at 60°, Wood (J. Anal. Chem. *1*, 138 (1887) at 30-40°, Meineke (Chem. Ztg. *20*, 108 (1896) at 50-60°, Gladding (J.A.C.S. *18*, 23 (1896), also Jörgensen (Z. f. Anal. Chem. *46*, 370 (1907) at 50°, Chesneau (Compt. Rend. *146*, 758 (1908) precipitates at 65-70° to avoid the formation of ammonium tetramolybdate. Artmann and Brandis (Z. f. Anal. Chem. *49*, *1*, (1910) use 50 cc. of solution, precipitate at 40-50°, a higher temperature causing adsorption of molybdenum as ammonium tetramolybdate. Hibbard (J. Ind. Eng. Chem. *5*, 998 (1913) uses 65° to prevent the separation of molybdic acid.

Artmann and Brandis believe that the rapidity with which the molybdate solution is added has a large influence. They add the solution dropwise. Gladding makes a point of adding the solution slowly and stirring. Rapid addition causes adsorption of molybdic acid. Artmann and Brandis also allow the precipitate to stand in contact with the solution for an hour and a quarter only at 40°, not longer, in order to avoid adsorption of molybdenum.

Washing. Gladding washes with 1% nitric acid solution then water. Chesneau, Woy, Jörgensen, and Christensen (Z. f. Anal. Chem. *47*, 529 (1908) use an ammonium nitrate, nitric acid solution. Chesneau also uses water. Ishert and Stutzer (Z. f. Anal. Chem. *26*, 583 (1887) wash with ice cold water. Artmann and Brandis observed turbidity after washing with water which they claim was white ammonium tetramolybdate and contained no phosphorus.

In the present investigation the most satisfactory wash solution was found to be one containing 10 grams of ammonium nitrate and 5 cc. of concentrated nitric acid per liter. A 1% nitric acid solution can also be used. It was, however, not possible to wash the precipitate free of electrolyte with water or even ice cold water without causing it to pass through the filter. The portion which ran through was not white but yellow. Ice cold water is more satisfactory than water at room temperature. When it is desirous to wash the precipitate free of acid as in the acidimetric method dilute potassium nitrate or potassium chloride solutions proved satisfactory.

The following method is proposed for the precipitaiton of phosphorus as ammonium phosphomolybdate, and for the determination of phosphorus:

To a pure phosphate solution containing 20.35 mg. phosphorus in a volume of 120 cc., 5 g. of ammonium nitrate are added. To

the cold solution are added rapidly 45 cc. of molybdate solution (15 cc. of solution I poured into 30 cc. of solution II). After stirring the solution for a few minutes the precipitate forms and settles rapidly. This is allowed to stand from 4 hours to 24 hours. It is often convenient to filter the day after precipitating. For less phosphorus less molyddate solution may be used. The precipitate is dissolved in 10 cc. of ammonium hydroxide and the phosphorus precipitated with magnesia mixture under the usual conditions and weighed as magnesium pyrophosphate.

The completeness of precipitation of the phosphorus as ammonium phosphomolybdate was tested by dissolving the precipitate in ammonium hydroxide and precipitating the phosphorus with magnesium acetate solution as described above.

P calculated from KH_2PO_4 taken	P calculated from $Mg_2P_2O_7$ found	Difference
.0251 g.	.0248 g.	—.0003 g.
.0232	.0229	—.0003
.0281	.0281	.0000
.0241	.0240	—.0001
.0490	.0489	—.0001
.0457	.0457	.0000
	Average deviation.....	.0001

To test the effect of chloride and sulphate in solution on the precipitation of phosphorus the following experiments were performed:

1. To a pure phosphate solution as above 5 grams of ammonium chloride were added and 45 cc. of molybdate solution (15 cc. of the ammonium molybdate solution I poured into 30 cc. of dilute hydrochloric acid 4:6). After filtering and washing the precipitate it was dissolved and the phosphorus precipitated with magnesia mixture.

2. Same as 1 except that nitric acid was used in the molybdate precipitating reagent.

3. In this case the phosphate solution contained 5 grams of ammonium sulphate and the precipitating reagent was the one described in this paper and the same as in 2.

The following results were obtained:

Method	P calculated from KH_2PO_4	P calculated from $Mg_2P_2O_7$ obtained	Difference
1	.0240 g.	.0239 g.	—.0001
2	.0244	.0243	—.0001
3	.0259	.0258	—.0001
3	.0240	.0239	—.0001

In view of the great variations in the results of precipitates that were dried it is useless to weigh the ammonium phosphomolybdate precipitate. It is therefore necessary to determine phosphorus in another way. Hence analyses were made on precipitates without drying them. The precipitates were obtained from known weights of phosphorus as follows:

1. To the pure phosphate solution 5 grams of ammonium nitrate were added in a volume of 120 cc. To this cold solution 45 cc. of molybdate reagent (15 cc. of solution I poured into 30 cc. of solution II) were added rapidly. After the precipitate stood it was filtered, washed with the ammonium nitrate, nitric acid solution, dissolved in ammonium hydroxide and reprecipitated with nitric acid after adding 2 cc. of ammonium molybdate solution in the same volume as in the first precipitation. After standing again it was filtered and washed as before, then dissolved in ammonium hydroxide and analysed as described previously in this paper.

2. Same as 1 except that 5 grams of ammonium chloride were added in place of ammonium nitrate.

3. Same as 1 except that 5 grams of ammonium sulphate were added in place of ammonium nitrate.

4. Same as 1 except that 5 grams of ammonium cholride were added in place of ammonium nitrate and hydrochloric acid was used in the molybdate reagent in place of nitric acid.

5. Same as 1 except that sulphuric acid was used in the molybdate reagent in place of nitric acid.

The following results were obtained:

Exp.	Method	P calculated from KH_2PO_4	P calculated from $Mg_2P_2O_7$ obtained	Molecular Ratio
1	1	.0280 g.	.0277 g.	1:24.61
2	1	.0233	.0230	1:24.63
3	2	.0239	.0237	1:24.43
4	2	.0241	.0238	1:24.64
5	3	.0354	.0351	1:24.35
6	4	.0229	.0228	1:24.41
7	4	.0239	.0237	1:24.54
8	5	.0234	.0232	1:24.33
9	5	.0243	.0240	1:24.54
			Mean molecular ratio	1:24.50

These experiments show that the presence of chloride or sulphate in solution has no effect on the completeness of the precipitation of phosphorus and also that the yellow precipitate obtained under these conditions is one in which the ratio of phosphorus pentoxide to molybdic oxide is constant. The average deviation of the above ratios is 5 parts per 1000. The results, however, do not agree with the generally accepted formula where the ratio of phosphorus pentoxide to molybdic oxide is 1:24.

THE VOLUMETRIC METHOD

By referring to the introduction it will be seen that the acidimetric titration method for the determination of phosphorus has always been surrounded by considerable uncertainty. These uncertainties involve the choice of factor which of course depends upon the composition of the ammonium phosphomolybdate precipitate, whether or not the ammonia is to be removed before making the titration and the choice of the indicator for the determination of the end-point. Furthermore, when phenolphthalein, which is the indicator most generally proposed, is used it is always a difficult matter to decide when the end-point is reached as the change in the indicator is very gradual.

In order to proceed intelligently in establishing the conditions for the acidimetric titration, electrometric titrations were made on solutions containing 5 mg. of phosphorus. The precipitate was dissolved in a known volume of standard sodium hydroxide, free of carbonate, placed in a cell and the hydrogen ion concentration measured at 25°C. by the Saturated Potassium Chloride Calomel Cell Method as described by Fales and Mudge (J.A.C.S. *42*, 2434 (1920).

After equilibrium was established, 0.25M sulphuric acid was added in successive portions and the potentiometer read after stirring the solution. About five minutes elapsed between readings. It was not possible to wait for the solution to come to equilibrium after each addition of acid, for the voltage changed continuously for several hours and the solution finally turned blue. The curves given below were obtained from the following data by plotting cubic centimeters of acid added as abscissa and voltages as ordinates.

These titrations were repeated on similar solutions from which the ammonia had been removed, before titration, by boiling in a current of hydrogen. (See curve II).

Data for Curve I

(Solution contained 5 mg. of Phosphorus, titration made in presence of the ammonia.)

cc. acid added	voltage	cc. acid added	voltage
0.0	.9605	4.0	.8269
0.5	.9540	4.2	.7979
1.0	.9490	4.4	.7628
1.5	.9436	4.6	.7019
2.0	.9374	4.8	.6630
2.5	.9290	5.0	.6395
3.0	.9160	5.2	.6275
3.2	.9088	5.4	.6196
3.4	.8986	5.6	.6110
3.6	.8832	6.0	.5919
3.8	.8574		

Data for Curve II

(Solution contained 5 mg. of Phosphorus, titration made after removing the ammonia.)

cc. acid added	voltage	cc. acid added	voltage
0.0	.9440	3.0	.7932
0.4	.9372	3.2	.7530
1.0	.9253	3.4	.6871
1.5	.9102	3.6	.6607
2.0	.8823	3.8	.6458
2.2	.8654	4.0	.6341
2.4	.8488	4.2	.6285
2.6	.8322	4.4	.6203
2.8	.8150	4.8	.6020

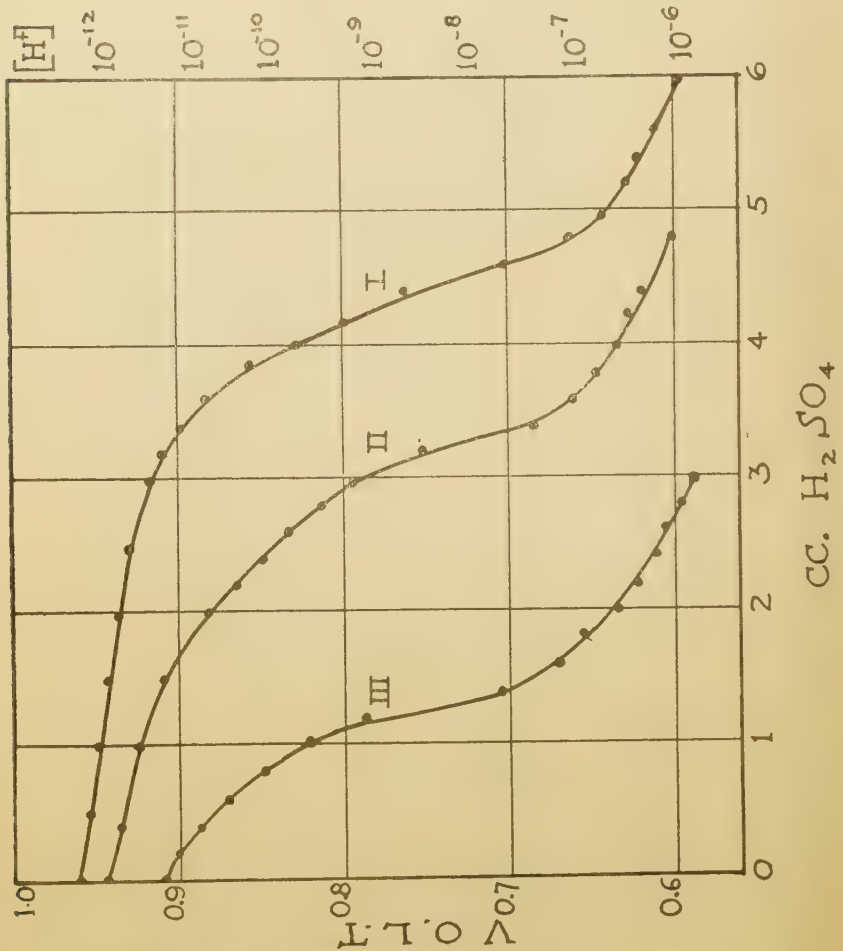
Data for Curve III

(Solution contained very little phosphorus.)

cc. acid added	voltage	cc. acid added	voltage
0.0	.9080	1.6	.6713
0.2	.8995	1.8	.6548
0.4	.8872	2.0	.6367
0.6	.8710	2.2	.6229
0.8	.8480	2.4	.6120
1.0	.8225	2.6	.6040
1.2	.7857	2.8	.5944
1.4	.7027	3.0	.5856

None of the curves shows a sufficiently pronounced point of inflection to yield a satisfactory color change in the indicator except in the case of Curve III. The rather indefinite point of inflection does occur in the phenolphthalein range and therefore shows that this is the best indicator for this titration. By comparing the curves made in the presence (Curve I) and absence of ammonia (Curve II),

it is seen that there is no advantage in its removal. The unsatisfactory form of the titration curve is certainly due to the presence of phosphoric acid. In the case of Curve III where the solution con-



tained very little phosphorus a more definite point of inflection was obtained showing that the method is more satisfactory for very small amounts of phosphorus.

That the difficulties encountered in titration were really due to the presence of phosphoric acid rather than ammonia, as is generally

assumed, was suggested by Fairchild (J. Ind. Chem. Eng. *4*, 520 (1912), who proposed its removal by precipitation with barium. It should also be noted that Hibbard (J. Ind. Eng. Chem. *5*, 998 (1913) attributed difficulties to the presence of both phosphoric acid and ammonia.

As a result of this work it has been shown that the determination of phosphorus in quantities of 10 mg. or over is best accomplished by precipitation with the ammonium molybdate solution which has been described and under the conditions which have been given. The precipitate obtained is dissolved and the phosphorus precipitated by magnesia mixture and weighed as $Mg_2P_2O_7$. For quantities of phosphorus less than 10 mg. the weighing of such small quantities of $Mg_2P_2O_7$ becomes inaccurate and the use of the acidimetric method is therefore advocated.

SUMMARY

1. A new determination of the ratio of phosphorus to molybdenum in the yellow phosphomolybdate precipitate has been made by a new method of analysis.

2. It has been shown that the composition of the ammonium phosphomolybdate precipitate after drying is so variable as to render the gravimetric determination of phosphorus by this method most unsatisfactory.

3. A new method of the precipitation of phosphorus as ammonium phosphomolybdate has been devised. When precipitated by this method the yellow phosphomolybdate precipitate as formed in solution shows a constant ratio of phosphorus pentoxide to molybdic oxide which is 1 : 24.50 with a mean deviation of 5 parts per 1000.

4. It has been shown that this ratio remains constant even when large concentrations of chloride or sulphate are present in the solution from which the phosphomolybdate forms.

5. It has been shown that under the conditions given for the formation of ammonium phosphomolybdate no complexes with sulphates or chlorides are produced.

6. Electrometric titrations of yellow phosphomolybdate precipitates have been made. The curves plotted from these results have not thus far appeared in the literature and have furnished a rational method for the acidimetric estimation of phosphorus with a determination of its limitations.

7. Accurate methods for the determination of phosphorus have been described with the limitations under which they can be used.

VITA.

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